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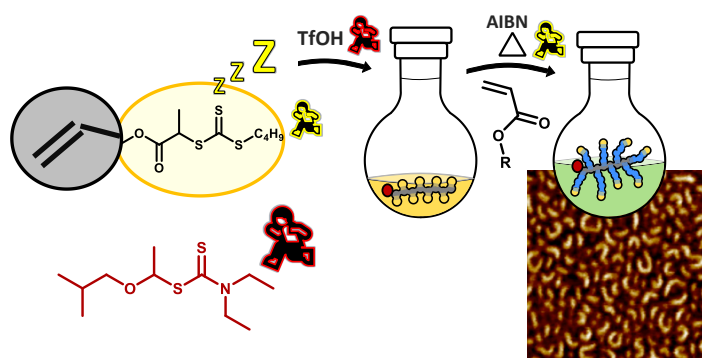
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Selective Cationic and Radical RAFT Polymerizations to Prepare Bottlebrush Polymers

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Abstract



Abstract

We report a novel orthogonal combination of cationic and radical RAFT polymerization to synthesize bottlebrush polymers using disparate RAFT agents. Selective consumption of RAFT agent is demonstrated to control cationic RAFT polymerization of monomer bearing a secondary dormant RAFT agent, subsequently allowing sidechain monomers to be grafted from the pendent RAFT agents by radical centered RAFT polymerization without intermediate purification.

Main text

In the recent years, the use of Reversible Addition Fragmentation Chain Transfer (RAFT) agents¹ in research have focused beyond traditional thermally initiated controlled radical polymerization.^{2, 3} One emerging theme is using RAFT agents to facilitate other classes of polymerization such as Anionic Ring Opening Polymerization (AROP)⁴⁻⁶ and cationic (RAFT) polymerization to enable dual copolymerization strategies with radical centered RAFT polymerization,⁷⁻¹⁴ allowing unique copolymers compositions.^{6, 8} Another emerging theme is exploiting the versatile photochromic behavior of RAFT agents for photo-controlled polymerization upon photo-fragmentation of the R-group by UV-Vis irradiation directly (iniferter)^{15, 16} or through a photocatalyst (photoinduced-electron/energy transfer).¹⁷ In particular, Xu and Boyer demonstrated the wavelength dependency to selectively photo-activate RAFT agents^{16, 18-21} to permit selective RAFT control for orthogonal polymerizations, where an unselected yet activatable RAFT

agent remains dormant during selected photo-controlled radical polymerization,²²⁻²⁵ such selective RAFT process has previously been untapped due to undesirable chain transfer.²⁶

To this end, orthogonal iniferter-RAFT polymerization of methacrylic monomer bearing a secondary RAFT agent which remains intact during the polymerization of the methacrylic unit was demonstrated by Matyjaszewski *et al.* The pendant RAFT agents from the main chain polymer, can successively graft a second monomer to form the side chains by a second RAFT polymerization to furnish the bottlebrush polymer ('grafting-from' approach) (**Fig. 1**).²³ However, using this approach for bottlebrush synthesis requires thorough intermediate purification to remove unreacted RAFT agent functional monomers prior to the second RAFT polymerization.

In the current literature, orthogonal polymerizations through selective RAFT process has only been demonstrated with photo-controlled methacrylate polymerization where RAFT agents bearing acrylic-based R-group remains dormant.²²⁻²⁵ Moreover, photo-control rely on photons of different wavelength, which are prone to undesirable 'cross-over' due to overlapped photoresponse.^{27, 28}

An alternative approach to orthogonal RAFT control is through selective cationic and radical chain transfer using disparate RAFT agents. Whilst the literature has primarily focused on one common RAFT agent to facilitate both cationic and radical chain transfer to allow interconvertible cationic and radical RAFT copolymerization,^{2, 9, 28} in these systems, lack of cationic RAFT chain extension is typically observed from acrylic terminal RAFT polymer. This can be explained by the incompatible cationic fragmentation of the R-group which bears an electron withdrawing group (EWG).^{10, 11} In contrast, EWGs can favor radical fragmentation as it increases radical stabilization energy.^{10, 29}

Here we demonstrate novel selective RAFT process to permit orthogonal polymerization in absence of external control (e.g. light). Specifically, one RAFT agent to selectively control cationic polymerization of vinyl ether monomer bearing a second RAFT agent which remains dormant from cationic chain transfer events. The pendent RAFT agent enables successive radical-centered RAFT polymerization, allowing synthesis of structurally well-defined bottlebrush polymers. Finally, the two polymerizations were demonstrated tandemly in one-pot without intermediate purification.

Dual selective cationic and radical RAFT polymerization system was realized by employing 1-isobutoxyethyl diethylcarbamodithioate (IBDTC) to control the cationic polymerization of 4-(vinylloxy)butyl 2-(((butylthio)carbonothioyl)thio)propanoate (VBBTP), followed by the radical polymerization of acrylic monomers controlled by the VBBTP side chains (**Fig. 1**). IBDTC was selected as the cationic RAFT agent due to its favorable fragmentation of the carboxonium R-group and excellent cationic chain transfer properties of dithiocarbamates arising from the Z-group.⁹ VBBTP was designed to combine high reactivity of trithiocarbonates towards radical addition³⁰ and radical stabilizing electron-

withdrawing R-group for highly effective radical fragmentation^{31, 32} but incompatible for cationic fragmentation (**Scheme 1**).^{10, 11}

Following closely to the previously reported condition for cationic RAFT polymerization,⁹ VBBTP was cationically polymerized in DCM at - 48°C using TfOH as the initiator at fixed molar concentrations ([VBBTP] = 0.5 M, [TfOH] = 1 mM). Range of Degree of Polymerization (DP) of PVBbTP_n (n = 10, 24, 45, 143) was targeted by changing the molar ratio of [VBBTP]/[IBDTC], taking into the account chains generated from TfOH initiation (**Fig. 2, Table 1**). Completion of the polymerization was confirmed after 10 minutes by ¹H-NMR spectroscopy from the disappearance of vinylic proton (δ = 6.41 – 6.50 ppm, **Fig. S1**) indicative of quantitative monomer conversion in all cases. For work up, these were first quenched with methanol and triethylamine mixture and precipitated into methanol. Pleasingly, Size Exclusion Chromatography (SEC) of PVBbTP_n analysis shows appreciably narrow monomodal molar mass distribution (\mathcal{D} = 1.14 – 1.37, **Table 1**) and shift towards higher molar mass with increasing [VBBTP]/[IBDTC] ratio (**Fig 2**). It is important to note, the experimental number average molar mass $M_{n,SEC}$ based on SEC analysis poorly reflects targeted theoretical number average molar mass $M_{n,th}$ due to differences in hydrodynamic volume with polystyrene standards in this work; however, the systematic difference in $M_{n,SEC}$ is indicative measure for molar mass control. Importantly, the quartet signal at δ = 4.76 - 4.85 ppm which corresponds to C-H of the R-group adjacent to the trithiocarbonate (H_h , **Fig. S1, Fig. 3**) has the expected 1:2 ratio (by integration) with VBBTP C-H₂ signal at δ = 4.09-4.22 ppm (H_f , **Fig. S1, Fig. 3**), confirming complete absence of chain transfer of VBBTP side chains during cationic polymerization. Furthermore, end group signals from carboxonium initiation (H_p , **Fig. 3**) and the terminal vinyl-ether next to the dithiocarbamate (H_{b*} , **Fig 3**) is indicative of selective consumption of IBDTC.

Poly(methyl acrylate) (PMA) side chains were then grafted from the PVBbTP_n by radical RAFT polymerization from the VBBTP side chains. DP of the PMA sidechains were determined by the monomer conversion and initial molar ratios of MA to the VBBTP side chains ($DP_{PMA} = MA \text{ conversion} \times [MA]_0/[VBBTP]_{sc}$). These were all carried out at 70 °C, using AIBN as the radical initiator ($[VBBTP]_{sc}/[AIBN]_0 = 20$). To prevent the formation of intermolecular brush-brush by bimolecular radical combination of growing side chains, the polymerizations were stopped at low monomer conversions (**Fig. S3, $p < 62\%$, Table S2**).³³ In all cases, SEC analysis shows a clear evolution of monomodal molar mass distribution PVBbTP_n-g-PMA_m from the respective PVBbTP_n scaffolds (**Fig. 4**).

PVBbTP₁₀-g-PMA₈ bearing short PMA sidechains (DP = 8) was synthesized and isolated by precipitation into hexane for end group analysis by ¹H-NMR spectroscopy (**Fig. 3**). Quantitative grafting efficiency from VBBTP side chains was evident from complete disappearance of the aforementioned quartet C-H peak corresponding to the R-group (H_h , **Fig. 3**) replaced by terminally inserted MA at δ = 4.95 - 4.87 ppm ($H_{u-terminal}$, **Fig. 3**). Importantly, the retention of terminal vinyl-ether C-H signal (H_{b*} , **Fig 3**, δ = 6.02 - 6.15 ppm) indicates lack of chain transfer of the backbone terminal RAFT end group during the radical polymerization of MA. This observation contrasts the previously reported photo-mediated orthogonal RAFT system, as the terminal trithiocarbonate on the methacrylic terminal end group would favor chain transfer with grafting acryl(ic/amidic) monomers.²³ We ascribe this unique high-end group fidelity as a Z-group effect,

due to the lack of acrylic radical addition to less reactive dithiocarbamates RAFT agents.^{30, 34} Thus, this unique feature highlights the scope for potential further work for RAFT selectivity.

To confirm topology of the molecular architectural control, PVBbTP₁₄₃ was grafted with DP 15 Poly(N-butyl acrylate) (PBA) side chains (PVBbTP₁₄₃-g-PBA₁₅, $M_{n,th} = 320 \text{ k gmol}^{-1}$, $M_{n,SEC} = 54 \text{ k gmol}^{-1}$, $\bar{D} = 1.42$, **Fig. 5A**, **Fig. S5**) was visualized by Langmuir Blodgett Atomic Force Microscopy (LB-AFM, **Fig. 5B**). The presence of dense linear cylindrical structures is consistent with bottlebrush prepared by our selective RAFT control.

Given the excellent ‘orthogonality’ observed for our system, tandem dual cationic-radical RAFT polymerization was then carried out in one pot, by sequential monomer addition (**Fig. 6B**) and as a one-shot selective polymerization VBBTP and MA (**Fig. 6C**).^{29, 35, 36} Final molar concentrations of $[MA]_0/[VBBTP]_0/[IBDTC]_0 = 6/0.25/0.01 \text{ M}$ was used for both cases to target the same backbone and side chain DP for comparison. To accommodate reactions for the dual cationic-radical RAFT system, toluene was used as a compatible solvent. In both cases, the initial cationic RAFT polymerization of VBBTP was quenched with MeOH/TEA after 20 minutes prior to the thermally initiated radical RAFT polymerization at 70 °C for 1 hour. In the case of sequential addition of MA, no additional solvent was added except for the AIBN as the stock solution. Successful formation of PVBbTP₄₅-g-PMA₁₇ by tandem radical RAFT from crude post-cationic RAFT mixture was indicated by SEC chromatograms, showing a clean shift from the PVBbTP₄₅ backbone (**Fig. 6B**, $M_{n,SEC} = 7.5 \text{ k gmol}^{-1}$, $\bar{D} = 1.18$) towards higher molar mass distribution (**Fig. 6B**, $M_{n,SEC} = 15 \text{ k gmol}^{-1}$, $\bar{D} = 1.15$, $p = 69 \%$), with no difference from PVBbTP₄₅-PMA₁₈ prepared by prior isolation of the PVBbTP₄₅ scaffold (**Fig. 6A**, $M_{n,SEC} = 20 \text{ k gmol}^{-1}$, $\bar{D} = 1.20$, $p = 75 \%$). On the other hand, one-shot tandem cationic-radical RAFT copolymerization of VBBTP and MA resulted comparatively slightly lower $M_{n,SEC}$ PVBbTP₄₅ (**Fig. 6C**, $M_{n,SEC} = 5.1 \text{ k gmol}^{-1}$, $\bar{D} = 1.23$) in spite of a quantitative monomer conversion (**Fig. S4**). The presence of small molecular weight species in the SEC chromatograms indicates early termination during cationic RAFT polymerization of VBBTP, possibly due to contamination of water arising from the MA as the comonomer mixture ($[MA]_0 = 60 \%$ vol), as aldehyde peak at 9.81 ppm is observed (**Fig. S4**). Subsequently grafting PMA sidechains ($p = 74 \%$) resulted in bimodal distribution, with a shift towards higher molar mass (**Fig. 6C**). Comparatively lower $M_{n,SEC}$ was obtained from deconvoluting the molar mass distribution ($*M_{n,SEC} = 10.5 \text{ k gmol}^{-1}$, $\bar{D} = 1.10$) due to shorter PVBbTP backbone and consumption of MA by early terminated PVBbTP species, which is observed as smaller broad PMA species ($*M_{n,SEC} = 2.8 \text{ k gmol}^{-1}$, $\bar{D} = 2.35$). We anticipate this can be further improved with sufficiently dried conditions.

In conclusion, we demonstrate a new form of orthogonal polymerizations by selectivity of two RAFT agents for cationic and radical chain transfer without external control. Selectivity was based on favorable cationic fragmentation of carboxonium and unfavorable cationic-fragmentation of radical stabilizing EWG bearing R-groups of the two RAFT agents. This enabled selective RAFT agent consumption for RAFT controlled cationic polymerization of monomer bearing a second RAFT agent which remains dormant towards cationic chain transfer. Subsequently second monomers were grafted from the pendent RAFT agents by radical RAFT polymerizations, allowing preparation bottlebrush in two steps without intermediate purification. Advancement of orthogonal polymerizations is valuable since it can simplify

the synthesis of complex macromolecular architectures such as bottlebrushes polymers,³⁷ where a combination of two polymerization steps is necessary to construct the backbone and the side chains in separate steps. Our new approach of selective RAFT process, can thus be further explored for future orthogonal experimental designs.³⁸

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

JT, PBT and WY were supported by the National Science Foundation under Award CHE-1808055. Authors acknowledges NMR-core technician member Marc A. ter Horst for training and NMR maintenance. Sally Lewis and Aaron Teator at UNC for THF-GPC maintenance. Frank Leibfarth and Travis Varner for valuable tips on cationic polymerization.

Table 1: PVBBTP_n obtained from selective cationic RAFT polymerization

Entry ^a	[VBBTP] : [IBDTC] : [TfOH] ^b	M _{n,th} (g mol ⁻¹) ^c	M _{n,SEC} (g mol ⁻¹) ^d	<i>D</i> ^d
PVBBTP ₁₀	10 : 1 : 0.02	3.6 k	2.7 k	1.14
PVBBTP ₂₄	25 : 1 : 0.05	8.3 k	4.8 k	1.25
PVBBTP ₄₅	50 : 1 : 0.1	16 k	7.3 k	1.37
PVBBTP ₁₄₃	200 : 1 : 0.4	48 k	11 k	1.34

^a. DP of PVBBTP_n determined by $p \times [\text{VBBTP}]/([\text{TfOH}] + [\text{IBDTC}])$, where p corresponds to monomer conversion determined by ¹H-NMR. ^b. relative equivalence with respect to fixed monomer initiator concentrations ([VBBTP] = 0.5 M, [TfOH] = 1 mM). ^c. M_{n,th} calculated from $\text{DP}_{\text{PVBBTP}} \times \text{MW}_{\text{VBBTP}} + \text{MW}_{\text{IBDTC}}$, where DP_{PVBBTP}, MW_{VBBTP} and MW_{IBDTC} corresponds to degree of polymerization of VBBTP and molar mass of VBBTP and IBDTC respectively. ^d. Determined from SEC-analysis (THF, dRI) using polystyrene standards.

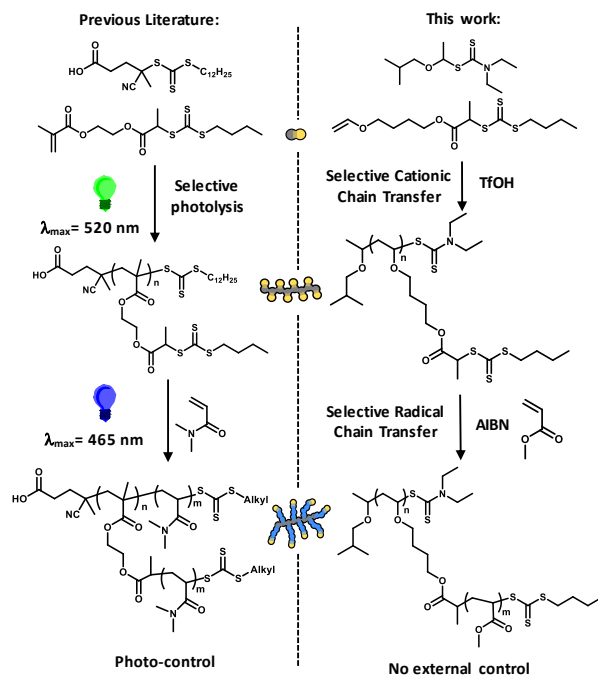
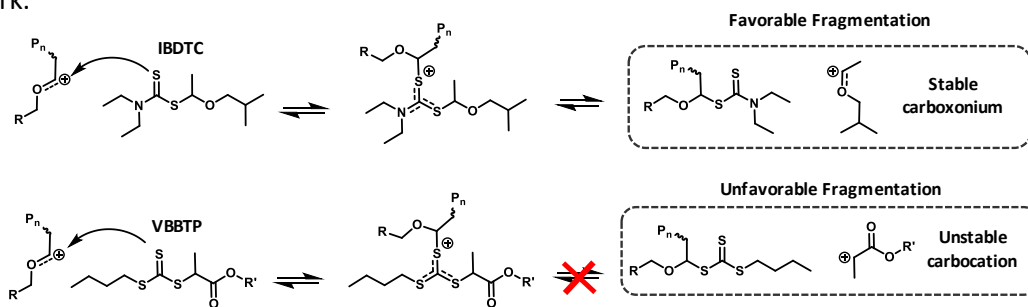


Figure 1. Comparison of two step synthesis of bottlebrush via orthogonal RAFT in previous literature and this work.

Scheme 1. Proposed selectivity between cationic RAFT polymerization of the two RAFT agents used in this work.



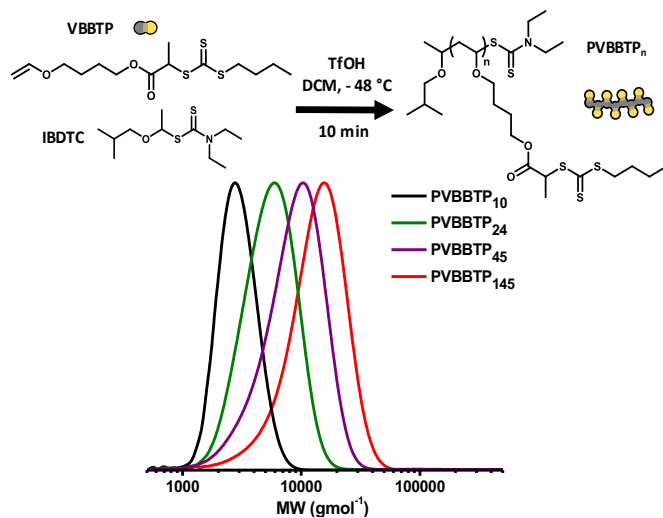


Figure 2. Differential molar mass distribution (THF-SEC, PSty standards) of PVBbTP_n (n = 10, 24, 45, **Table 1**) prepared by selective cationic RAFT of VBBTP controlled by IBDTC.

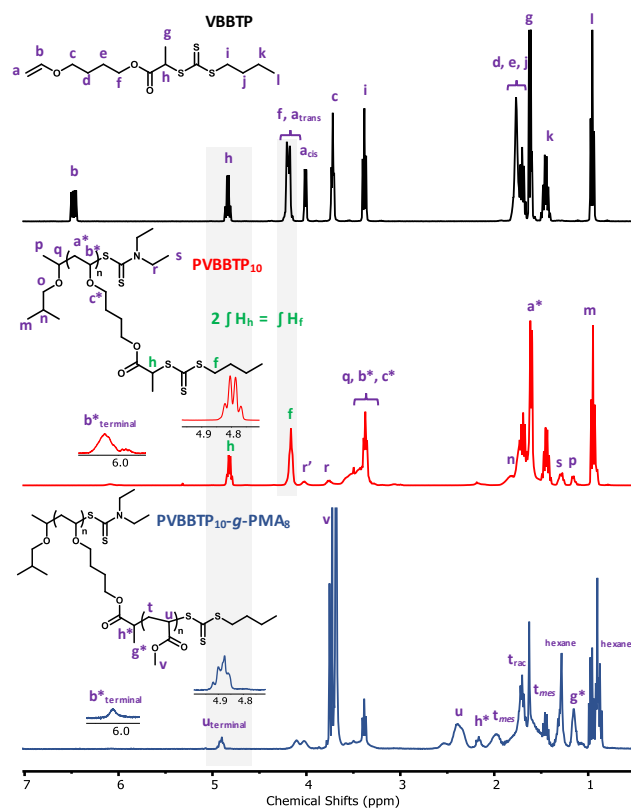


Figure 3. ¹H-NMR (CDCl₃) VBBTP monomer (black), PVBbTP₁₀ (red) and PVBbTP₁₀-g-PMA₈ (blue). Changes in chemical shifts are highlighted by asterisks.

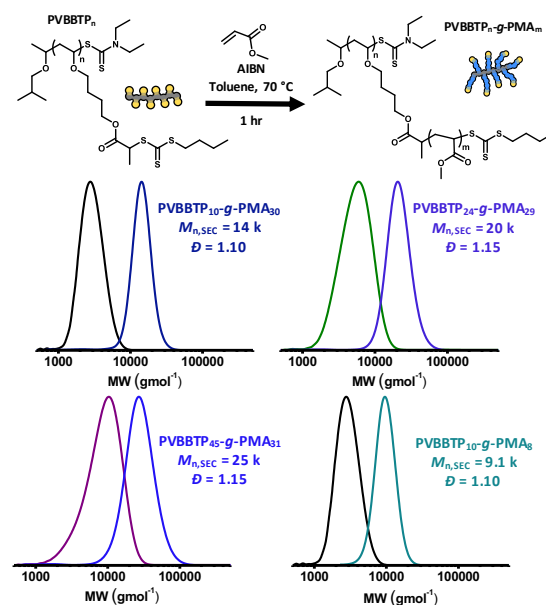


Figure 4. Differential molar mass distribution (dRI THF-SEC, PSty) of PVBbTP_n-g-PMA_m brush polymers (**Table S2**) prepared by grafting from VBBTP side chains from respective PVBbTP_n

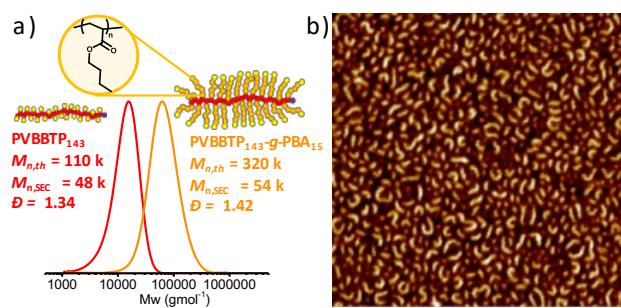


Figure 45. A) Molar mass distribution PVBBTP₁₄₃ (red) PVBBTP₁₄₃-g-PBA₁₅ (gold). B) LB-AFM image

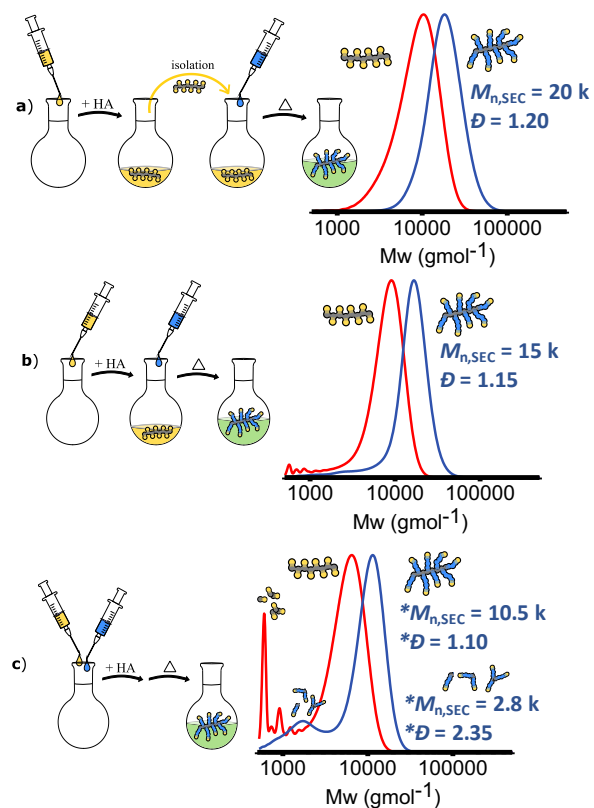


Figure 6. Comparison of molar mass distribution of PVBBTP₄₅-g-PMA_n (blue) grafting from PVBBTP₄₅ (red) via intermediate isolation (A), or tandemly carried out in one pot either by sequential addition of MA after polymerization of VBBTP (B) or selectively polymerizing VBBTP in presence of MA (C)

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